

THEORETICAL CONSIDERATIONS OF WATER-DIELECTRIC BREAKDOWN INITIATION FOR LONG CHARGING TIMES

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ABSTRACT

There are potential Naval directed energy applications that will require power amplifications from the pulsed power train on the order of 10,000 times. Traditional pulsed power trains often use separate components to form an energy store and a pulse forming line (PFL). However, mass and volume restraints for Naval applications require integration of these two functions into one, compact device. Water and water-based dielectrics are the materials of choice for the PFL that will provide the energy storage. The most important improvement needed for PFL's is increasing the electrical breakdown strength of water. This paper describes phenomena needed for a model of electrical breakdown initiation in water under long-term electrical stress. Dielectric saturation in the electric double layer, field-enhanced dissociation of the water molecule, field-enhanced ionic mobilities, field enhanced oxidation and reduction of the water molecule at electrodes, oxides patches on the electrodes, organic contaminants, surface contours and material phases are included in this survey. The goal is to be able to predict corrective treatments or procedures that increase the breakdown strength of water.

INTRODUCTION

The primary attributes needed by a PFL are high energy density to minimize mass and volume, and a long intrinsic time constant for minimum energy loss during storage. Other considerations are low cost, safety, and ease of use. Water is often the dielectric of choice to fulfill these requirements. High hold-off strength results in high energy density, because energy density is proportional to the square of the electric field. Thus, increasing the electrical breakdown strength of water yields great savings in mass and volume for PFL's. However, electrical breakdown is an extremely complex phenomenon. A complete theory on electrical breakdown in water would have to explain: the statistical behavior, different values for various electrode materials, variation of breakdown strength with electrical stress times, distribution of breakdown sites, dependence on non-breakdown conditioning shots, and the actual values of the electric field where breakdown occurs.^{1,2,3,4,5}

This paper theoretically investigates breakdown initiation in water for long charging times (i.e., effective stress time $\gg 10$ microseconds). In a sense, this investigation can be considered a subset of the more general problem of electrical

breakdown in any dielectric liquid. The excellent review by Sharbaugh⁶ summarizes the principal proposed mechanisms for electrical breakdown in liquids: electronic avalanche (similar to models for gases) and bubble theories (also called cavitation or low density region). This investigation attempts to delineate the various phenomena needed to construct a breakdown model, specifically for water dielectrics. For long charging times and gaps near a centimeter, electron avalanche seems unlikely; therefore, various modes that might explain the formation of low density regions are explored.

In this paper, the focus is on the electrode-water interface which is regarded as the weakest region for electrical hold-off by most of the recent literature. A series of electrochemical, double-layer phenomena (either intrinsic to the interface or associated with applied high voltage) are assembled into possible models resulting in the formation of low density regions immediately outside of the double layer (i.e., within about one micron of the electrode surface). While we concentrate on breakdown initiation, our explanations of breakdown initiation strive to be consistent with more traditional explanations of the actual breakdown process⁶.

A model of electrical breakdown should also attempt to describe sites on the surface of the electrode where this process is more probable. Oxide patches, organic contaminants in the double layer, surface contours and material phases should be considered in trying to reduce the model from a uniform process to a description of a finite number of potential breakdown sites on the electrode. The goal of this work is to describe the characteristics of potential breakdown sites well enough that either: corrective treatments or procedures for the breakdown sites can be implemented to increase the breakdown strength of water, or the sites may be identified for study with material science instruments (e.g., scanning electron microscopes, etc.) which may lead to new information useful for increasing the breakdown strength of water.

Summarizing, this paper describes potential models of breakdown initiation in water under long term electrical stress. The objective is to increase the breakdown strength of water and increase the utility of water-based pulse forming lines for pulsed power.

ELECTRIC DOUBLE LAYER AND DIELECTRIC SATURATION

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According to Bockris⁷, et al, the dielectric constant in the electric double layer of the water-electrode interface is approximately six or less. Under applied high voltage with a bulk field value of about 150 kV/cm, a Gauss's law calculation shows that the electric field in the double layer is on the order of 10^7 V/cm. Thus, fields in the double layer are considerably larger than bulk fields. The intrinsic electric field in the double layer is on the order of 10^7 to 10^8 volts/cm. These high electric fields induce saturation of the static dielectric constant. Work by Booth⁸ shows that the greatest decrease in the static dielectric constant also occurs around 10^7 volts/cm. Other effects in the double layer include field enhanced dissociation of the water molecule⁹, field enhanced ionic mobilities⁹, and field enhanced oxidation and reduction of water at the electrodes¹⁰. These effects mean that the double layer serves as the source for many more charged particles, with greater kinetic energy, than can be accounted for by conventional considerations of the bulk electric field.

Heating near the interfacial double-layer would occur not only as a result of inelastic collisions of charged particles but also by the recombination of excess dissociated hydronium and hydroxyl ions. While the energy released when hydronium and hydroxyl ions combine to form water molecules is about 13,300 calories per mole at 25°C, the energy required to boil water is only about 11,600 calories per mole.^{11,12} Thus, each ionic recombination contributes more than enough energy to vaporize a water molecule.

Also, gas will be evolving as the oxidation and reduction of water occurs. Hydrogen evolves at the cathode and oxygen at the anode. Furthermore, oxygen reactions with the anode electrode can be expected to occur. Thus, low density phases evolve at the interface and may contribute to the formation of a low-density region where breakdown can initiate and can also contribute to the growth of oxide layers on the anode.

The electric double-layer field arises because of the potential difference (PD) that is set up across the solid-liquid interface immediately upon contact. The total PD across the interface is the sum of the following: the PD arising from the change in potential from the surface of the metal to the interior (where the potential is constant) over the Thomas-Fermi length; the electron overlap potential of the lattice electrons extending into the liquid; the PD arising from the preferred orientation of the water dipoles; and the PD established by excess surface charges. The first three contributions are present even when the excess surface charge density is zero (the point-of-zero-charge or PZC)¹³. The magnitude of the double-layer field is typically on the order of tenths of Volts across roughly one nanometer resulting in magnitudes of 10^7 - 10^8 V/cm.

ENHANCED CONDUCTANCE

Kortum⁹ reviews the work started by Wien on the increase in conductance of electrolytes

at electric field strengths of the order of 10^4 - 10^5 V/cm. The ionic interaction and the degree of dissociation (for weak electrolytes) cause a considerable increase in conductance. The dissociation field effect in aqueous solutions of weak electrolytes results in an approximately linear increase in conductance for fields above 50 kV/cm. The magnitude of increased conductance is about 10% at 200 kV/cm for $\text{CH}_3\text{CO}_2\text{H}$. We have not found values for pure water in the literature. However, water is often considered the ultimate weak electrolyte and should respond in a similar fashion. Also, the field strengths at the double layer are near 10^7 V/cm, and the effect may be very important in this region.

SURFACE BREAKDOWN SITES

When trying to determine potential breakdown sites, regions of high electric field (and consequently high current density) are obvious candidates for sites that could generate a low density region sufficient to initiate breakdown. However, there are many types of sites to consider: sharp contours (e.g., whiskers, cracks, metallurgical features), oxide patches, adsorbed particulates and organic contaminants. Enhanced electric fields from sharp contours can be estimated by solving Poisson's equation. Oxide patches, particulates and organic contaminants are regions of low dielectric constant within the high-dielectric-constant water. Gauss's law predicts enhanced fields in these regions. The water-gap breakdown could be initiated by the local breakdown of a low-dielectric-constant surface feature. Thus, an important distinction that needs to be determined in attempting to derive improvements to the breakdown strength is: does the initiation arise from a low-density region in the dielectric liquid or does the initiation start in the local breakdown of a surface oxide patch or particulate or organic film?

RESULTS AND DISCUSSION

A possible strategy to increase the breakdown strength is suggested by the theoretical investigation of the interface. If the dielectric-filled gap between the electrodes is modeled as three reactances in series consisting of: the anode interface reactance, the bulk dielectric reactance, and the cathode interface reactance, then the electric field across the interface regions can be controlled by ensuring that sufficient conductivity exists at the interface to limit the potential drop at the interface. However, it may be that the classical concepts of reactance and conductivity are not applicable in the double-layer region. Also, note that this strategy assumes that the electric field at the interface dictates the breakdown behavior. Increased understanding of the quantum mechanical transfer of charge at the electric double-layer is necessary to implement this strategy.

Finally, the direct approach is to determine what processes, caused by the electric field near the interface, initiate breakdown. We are attempting to do this by

constructing a theoretical, breakdown "spotting scope". This is a numerical model that simulates various conditions (e.g., oxide patches, dielectric saturation, dissociation-recombination, surface contours, etc.) and estimates the effect on the liquid dielectric. The breakdown criteria is a low-density region, as in Sharbaugh⁶, of sufficient size to cause charge avalanche across the "bubble". Thus, the liquid does not breakdown directly. Rather, the "bubble" breaks down and launches a streamer across the dielectric.

We plan to perform several enlightening experiments within the next year to guide us in the development of the model. We plan to evaluate the effect on breakdown of oxide layers on common metals by evaluating gold-coated electrodes. We also plan to determine if organic contaminants and large particulates are affecting our breakdown results.

Our goal is to be able construct an applicable model of the breakdown process by use of these experiments, determine which actions or treatments will result in improvement of the breakdown strength, implement the changes and evaluate the effect of breakdown strength.

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